POSS POLYSTYRENE COPOLYMERS REACTIVITY AND CONTROL

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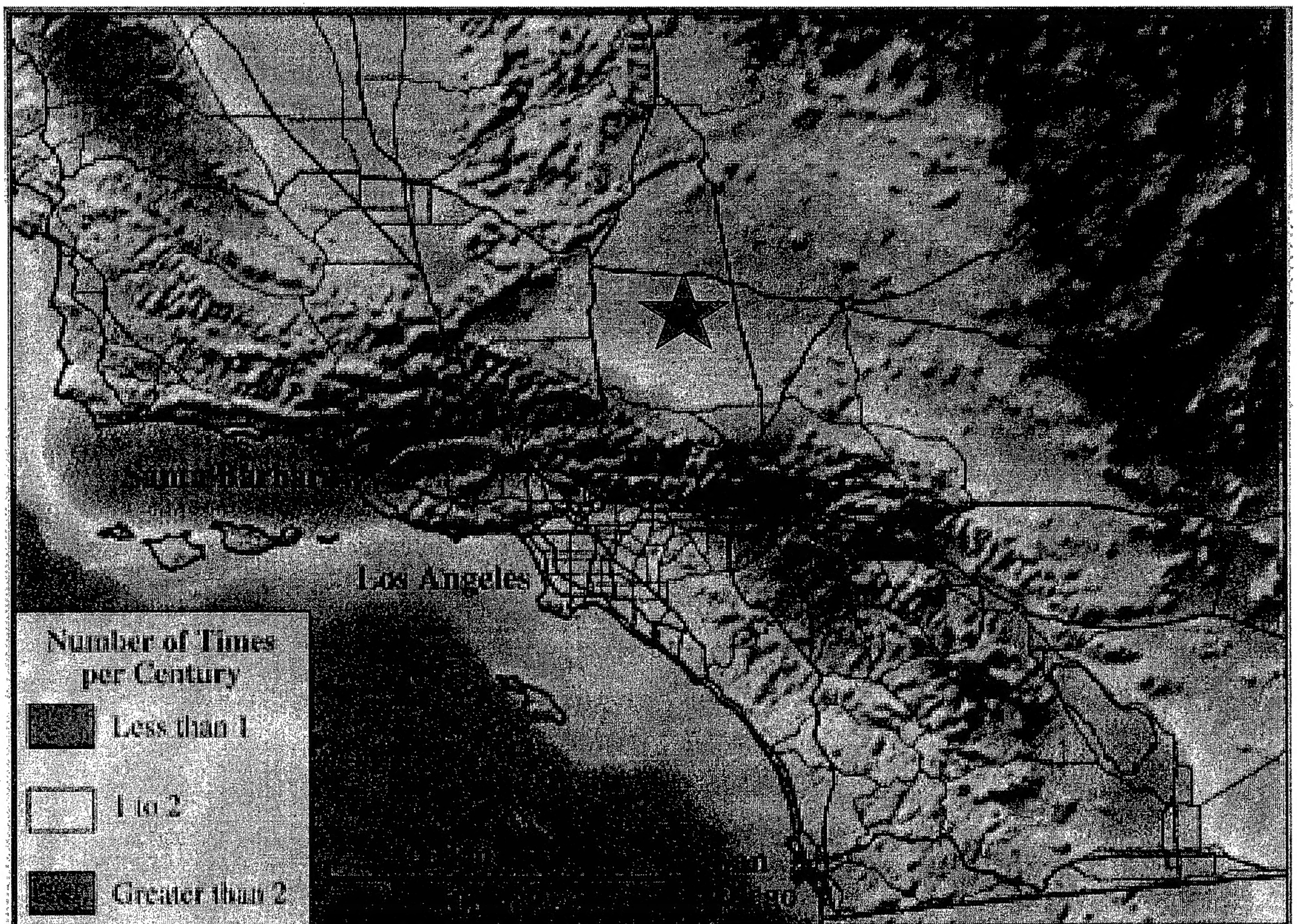
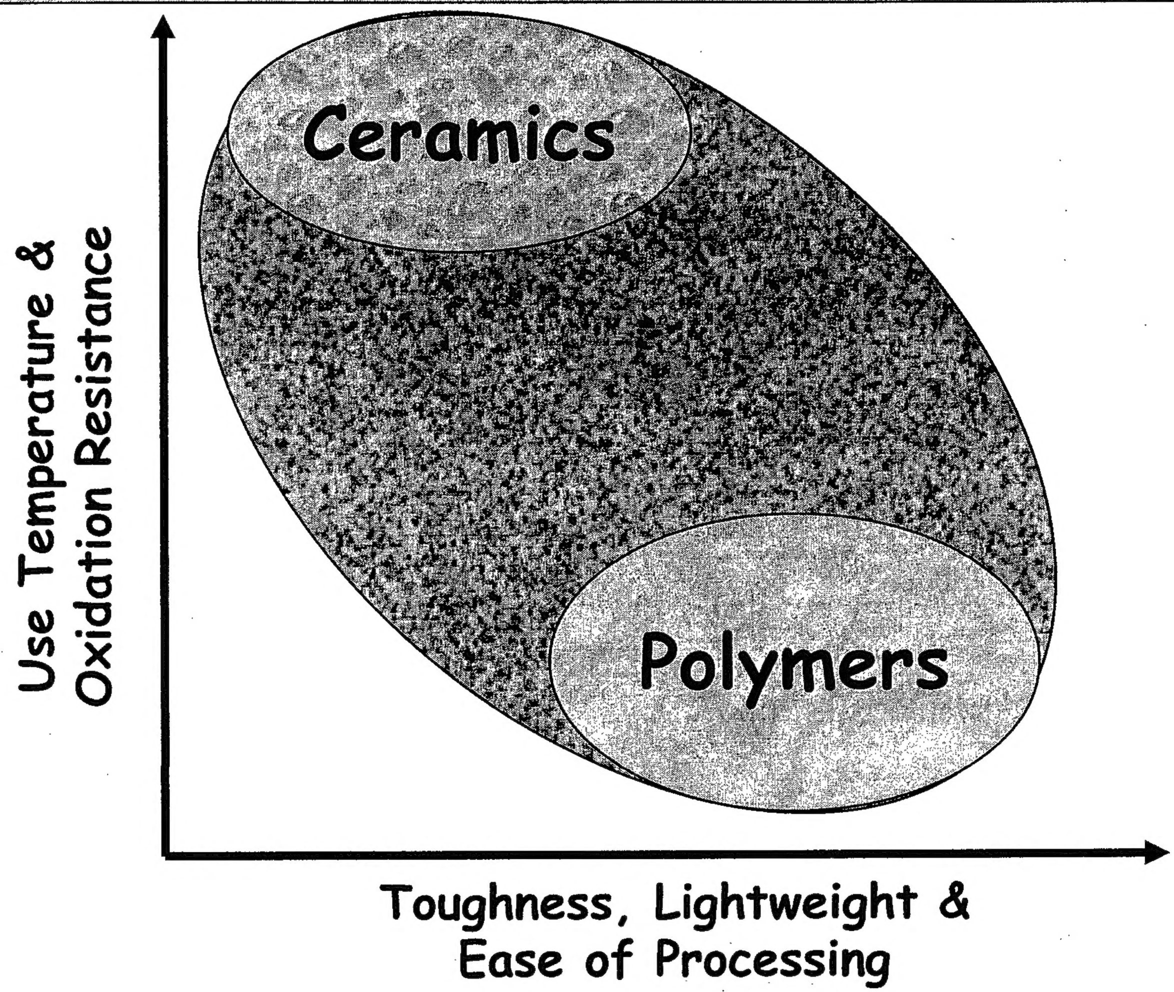
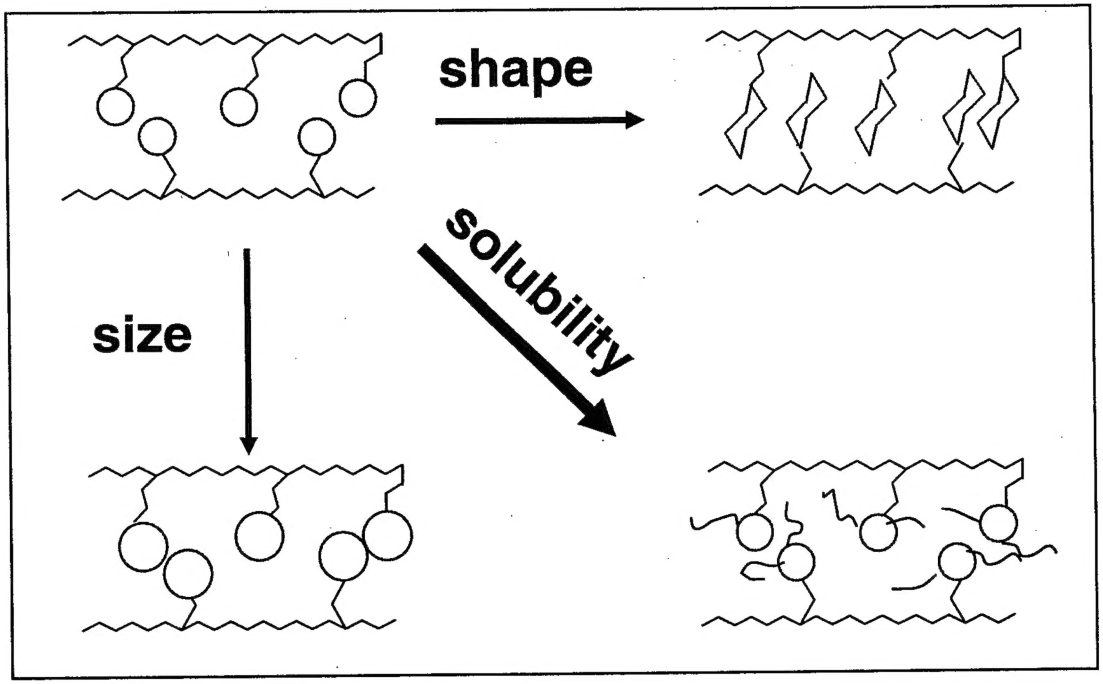


Hybrid Inorganic/Organic Polymers



- Hybrid plastics bridge the differences between ceramics and polymers

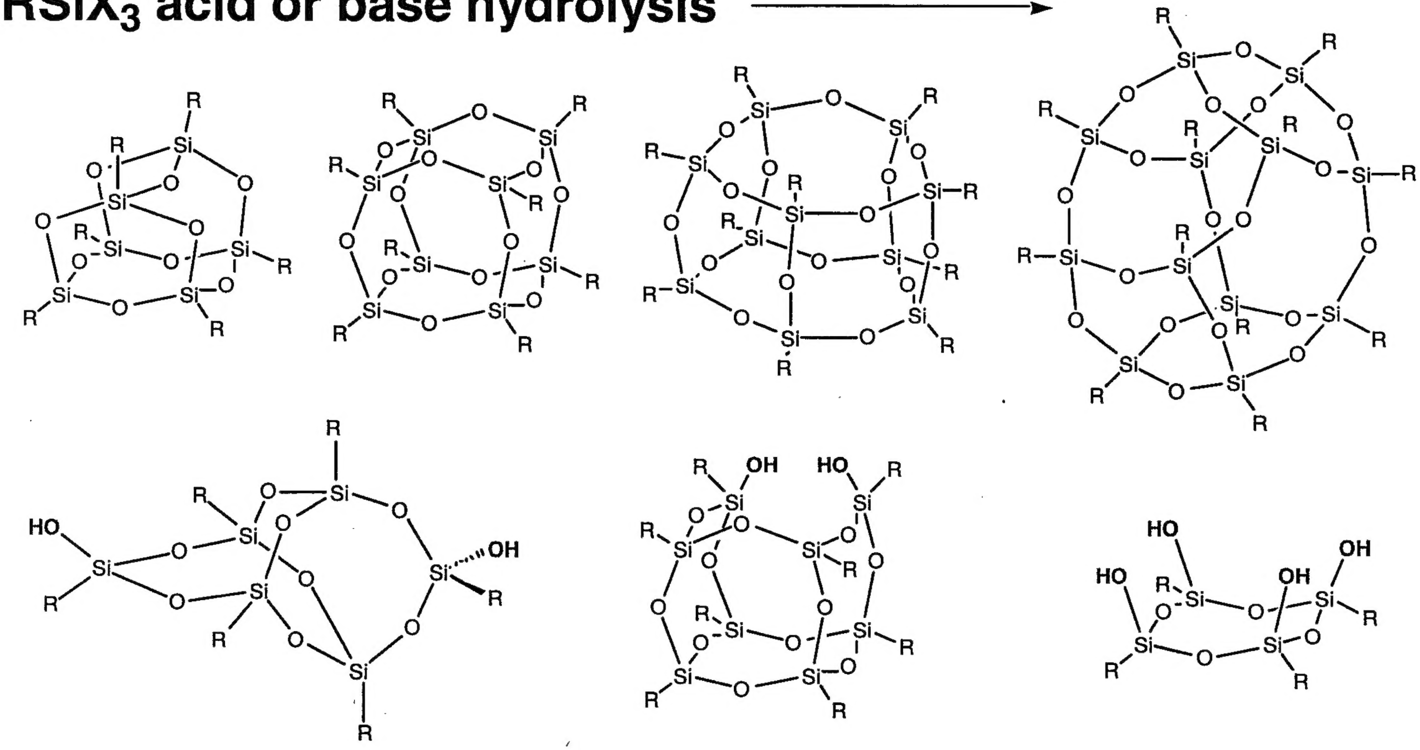
Structure-Property Relationships

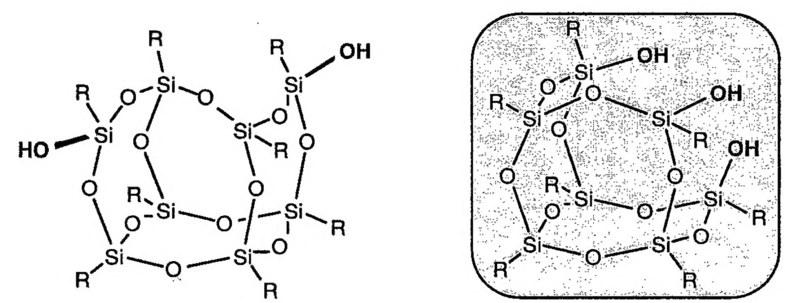


- Maximizing property enhancements through changes at the nano level
- Polymer miscibility vs. POSS/POSS interactions

POSS Synthesis

$RSiX_3$ acid or base hydrolysis →





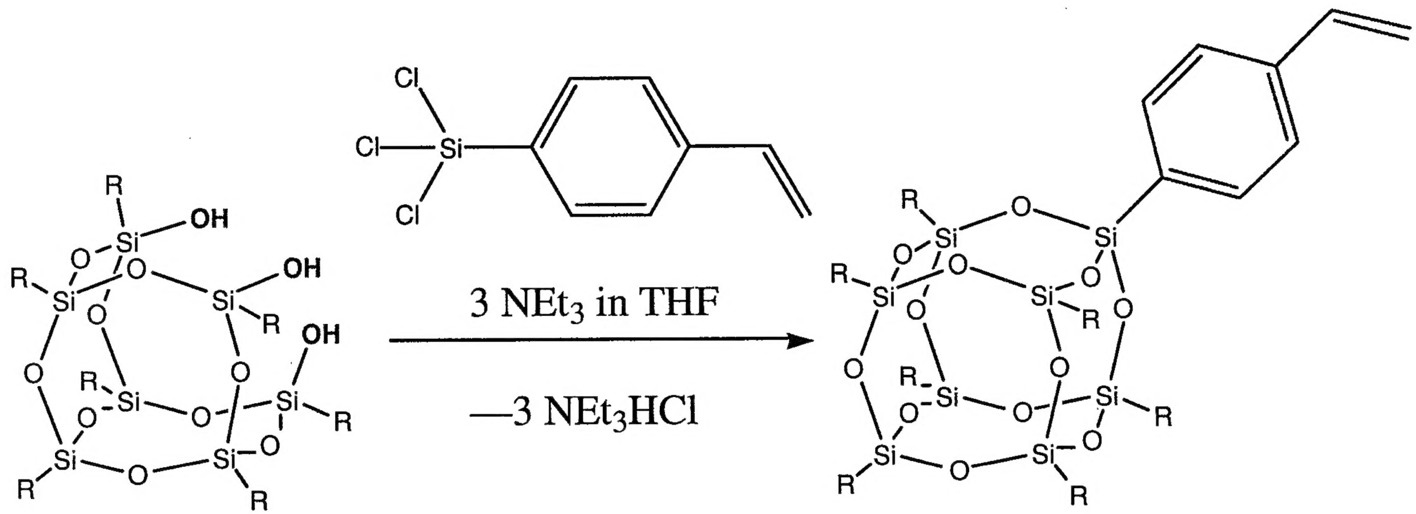
Brown & Vogt: JACS, 1965, 4313
Feher et al: JACS, 1989, 1741;
Organometallics, 1991, 2526;
Chem Comm, 1999, 1705, 2309

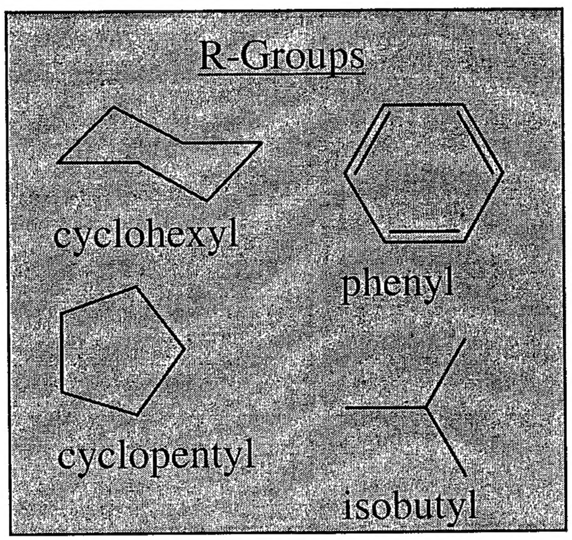
Introduction to POSS-Styrenes

POSS-styrene copolymers were first synthesized via solution polymerization in toluene. The solubility of cyclopentylPOSS styrene dictated that polymers with degrees of polymerization of about 200 were obtained. Thermal analysis of these polymers demonstrated an increase in Tg with POSS content and significant differences between cyclohexylPOSS and cyclopentylPOSS. Mechanical properties were poor as the materials were not very entangled. Although it was expected that random copolymers were being made, one copolymer (16 mole % CyclopentylPOSS) clearly showed two thermal transitions indicative of a block copolymer. It is possible that the apparent blockiness is caused by association of POSS groups from different unentangled polymer chains. Short length scale blocks have been seen in TEM images of random POSS polynorbornene copolymers. Bulk copolymerizations yielded materials with degrees of polymerization over 3000 and these highly entangled materials showed excellent mechanical properties. POSS-styrenes with DP's around 3000 form insoluble gels that is a function of POSS group. Because of all the aforementioned effects we have begun to accurately determine POSS-styrene reactivity ratios.

See slides 7 - 13

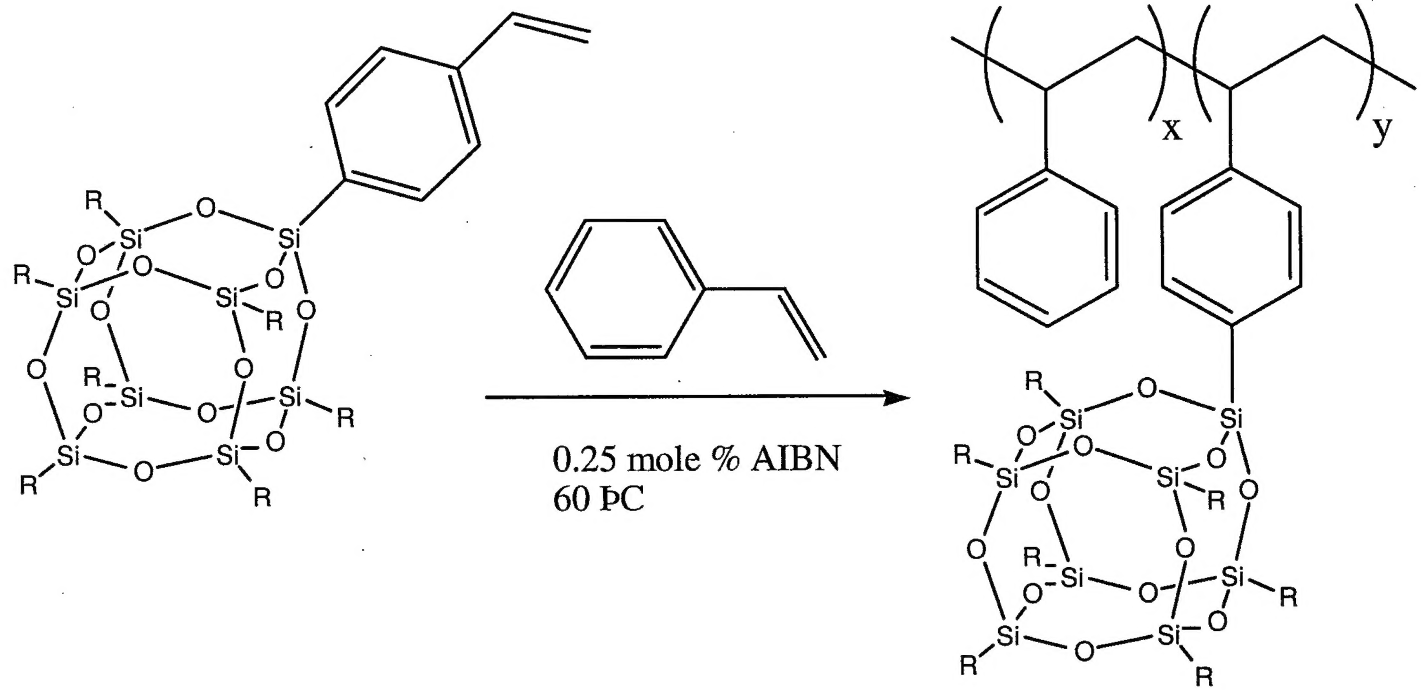
POSS-Styrene Monomer Synthesis





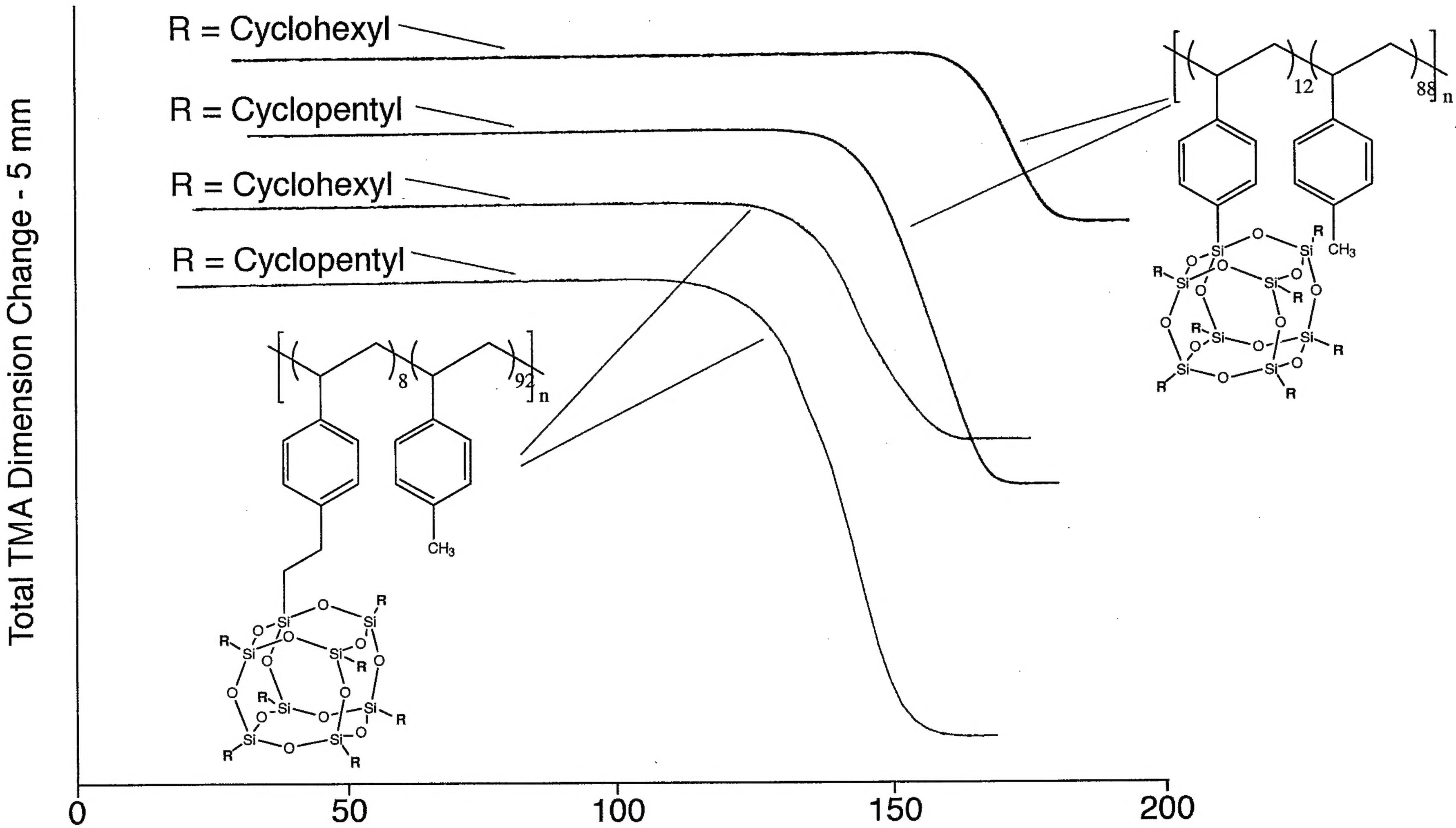
- High-yield syntheses
- Phenyl derivative requires inverse addition
- J. Inorg. Organomet. Polym., Vol 11, 2002, p. 155

POSS-Styrene Copolymer Synthesis



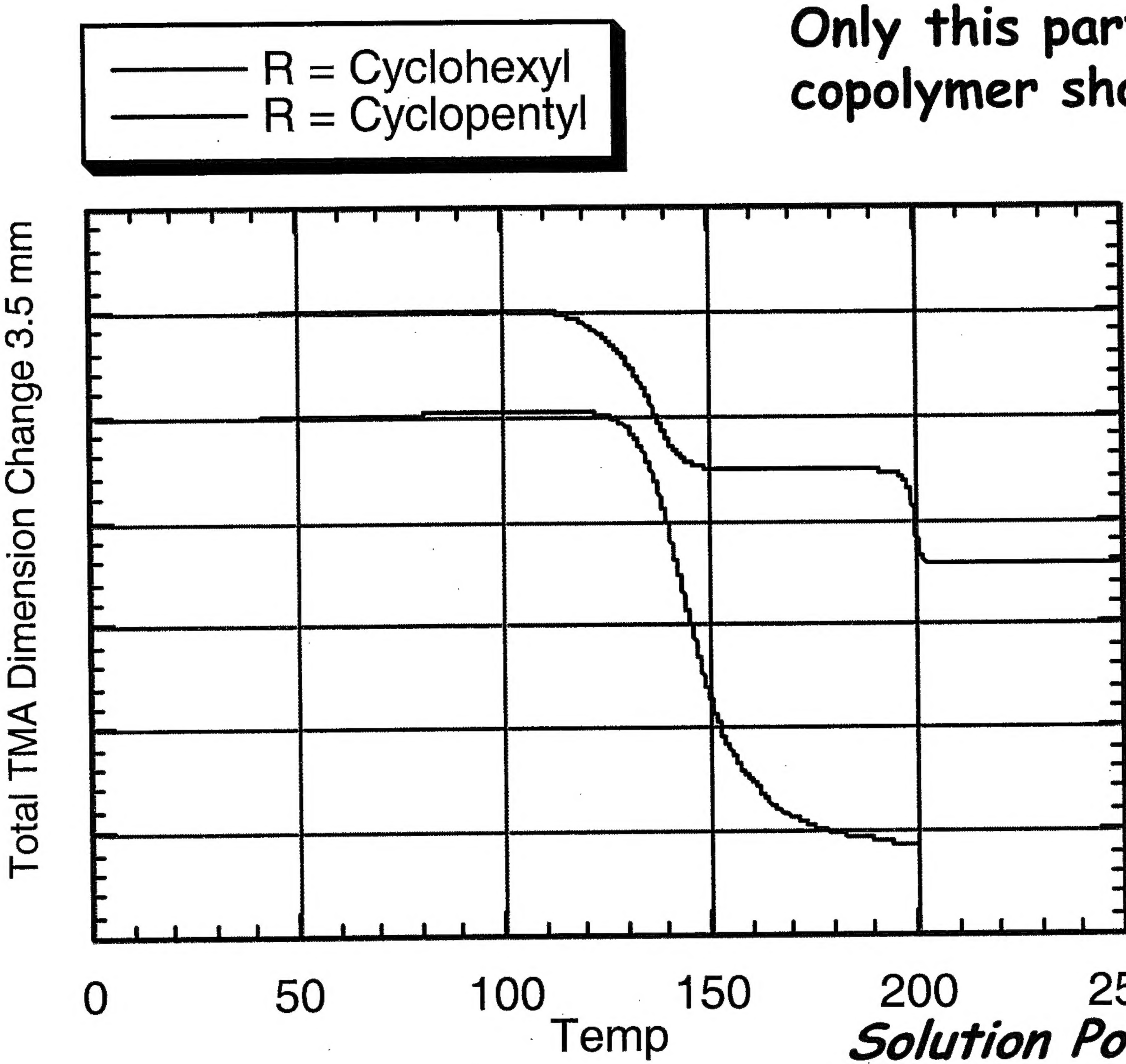
- Solution polymerization in toluene or bulk polymerization possible
- Polymerization is limited by solubility of the POSS-macromer
- Isobutyl-POSS is the most soluble, Phenyl-POSS the least soluble
- Macromolecules Vol. 29, 1996 p. 7302

TMA Comparison: POSS Group Effect

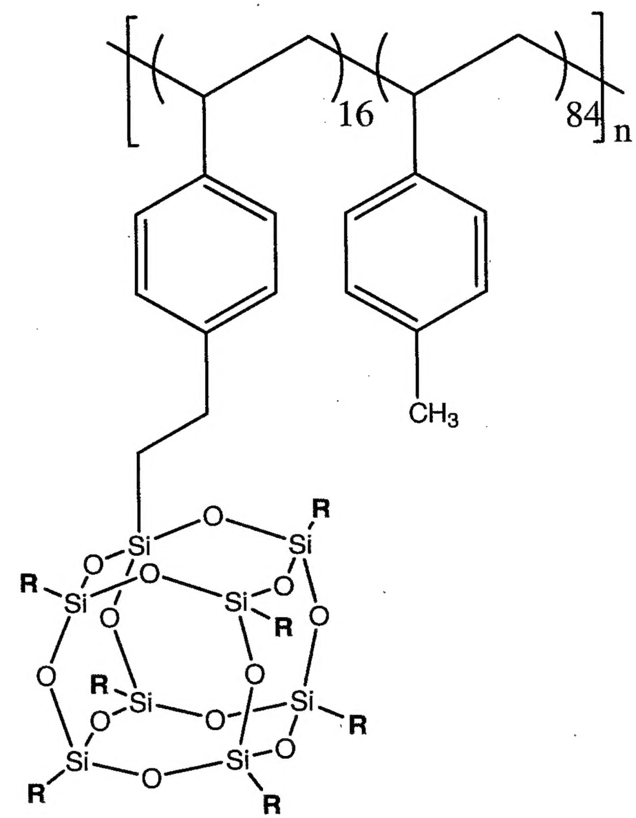


Solution Polymerized Materials

TMA Evidence for a Blocky Copolymer

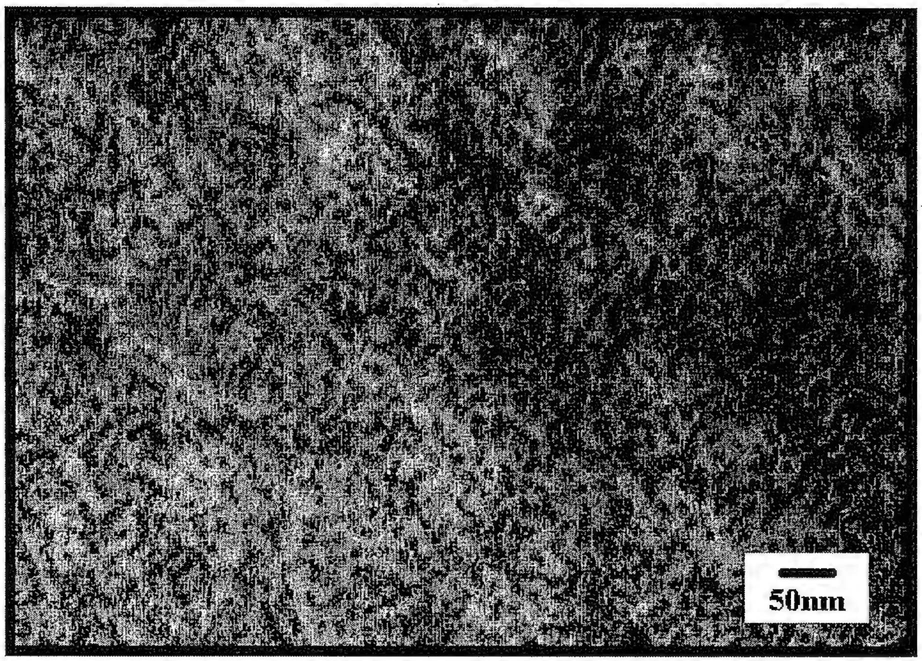


Only this particular cyclopentylPOSS copolymer shows two transitions.



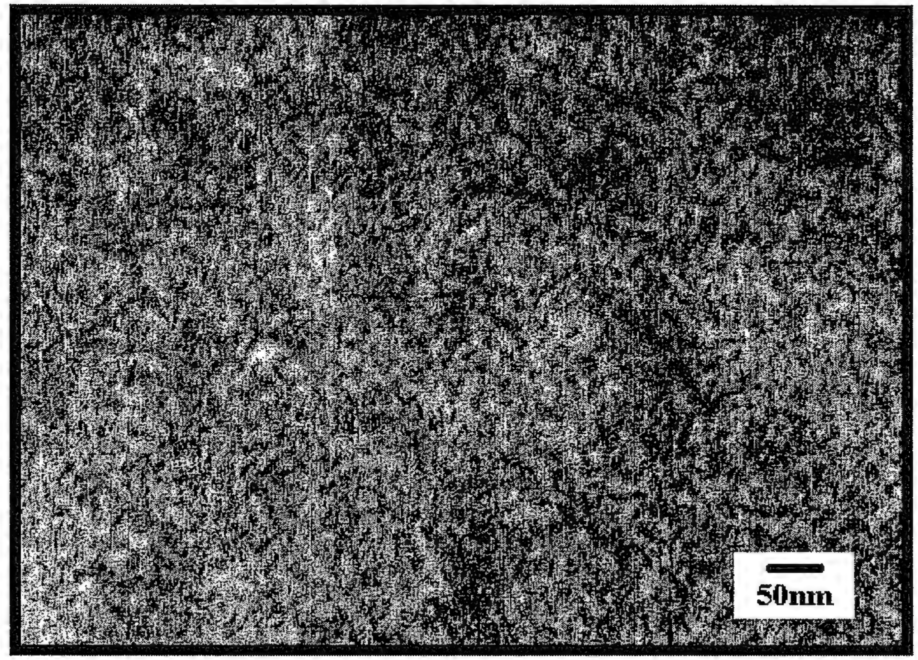
TEM of Random POSS Norbornenes

50CyPOSS/PN



"Coarse" Cylinder Nanostructure
(Diameter ~ 12nm)

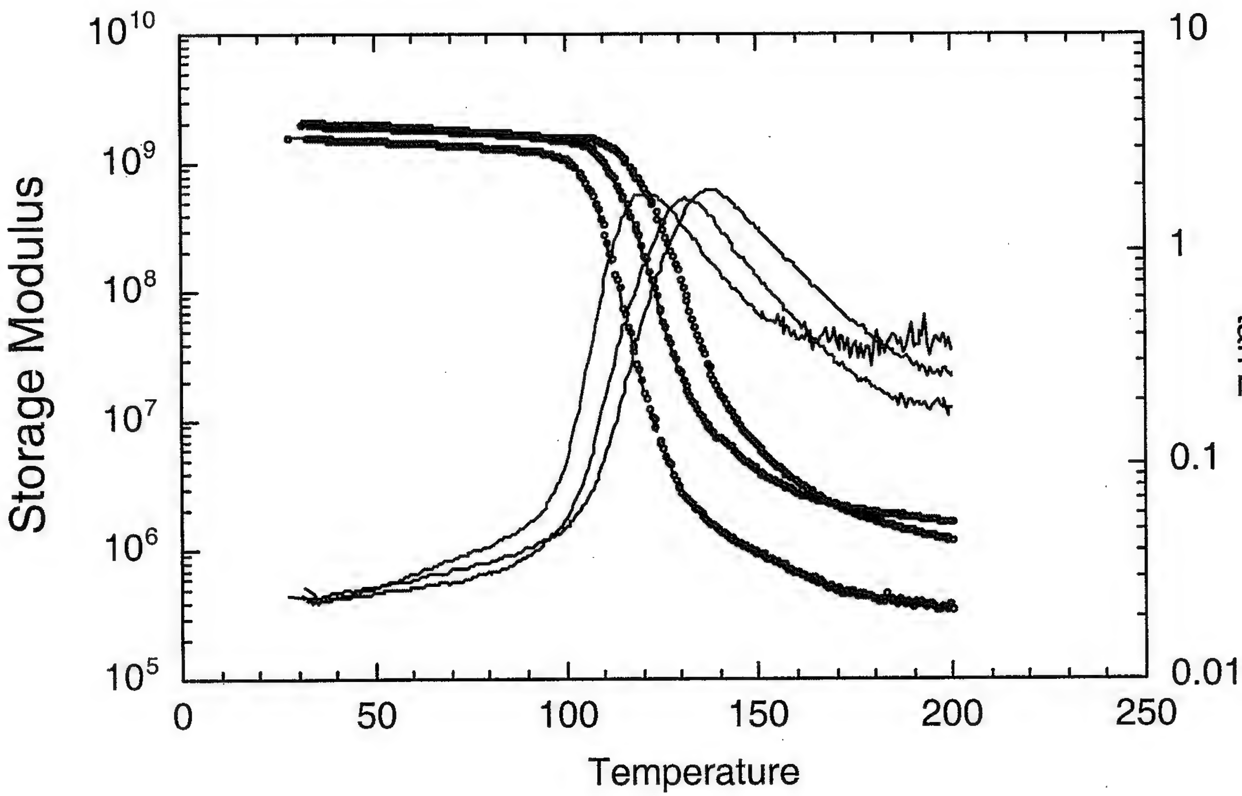
50CpPOSS/PN

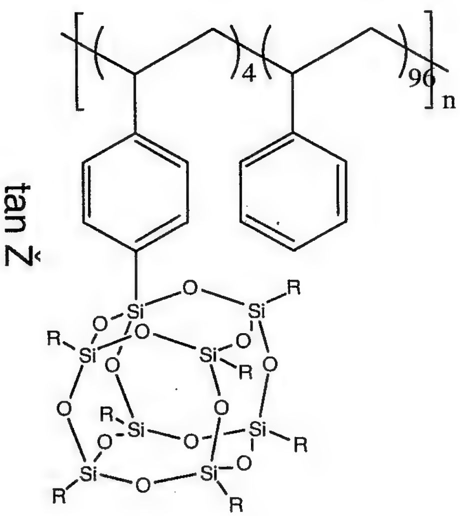


"Fine" Cylinder Nanodstructure
(Diameter ~ 6nm)

CyclohexylPOSS-rich domains may entrain more unoriented polynorbornene chains than CyclopentylPOSS-rich domains.

DMA of 30 Wt. % POSS-Polystyrenes

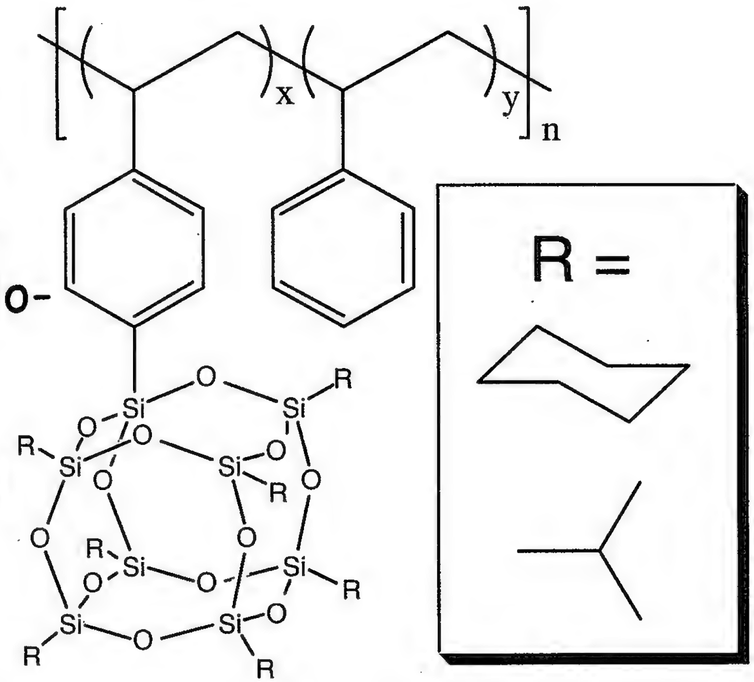




- Comparison of isobutyl, cyclopentyl & cyclohexyl
- High Molecular Weight Bulk polymerized samples

Solubility of High Molecular Weight Copolymers

Both bulk and solution polymerization methods were used to find that highly entangled POSS-polystyrene can form an insoluble gel. If the R-group is cyclo-hexyl, then this gel effect occurs at very low POSS content. Much higher loadings of isoButylPOSS are required to obtain similar insoluble materials.



POSS-POSS Interactions can Dominate to form insoluble "Gels"

POSS type	Degree of polymerization	Wt% POSS	Styrene/POSS
Cyclohexyl	> 3000	5-10	~150:1
isoButyl	~4000	35-40	~17:1

Reactivity Ratios for Styrene / POSS-Styrene

M_1: Styrene Monomer

M_2: POSS-Styrene Monomer

M_1^*: growing polymer M_1-radical

M_2^*: growing polymer M_2-radical

r_1: reactivity ratio for Styrene

r_2: reactivity ratio for POSS-Styrene

$$M_1^* + M_1 \xrightarrow{k_{11}} M_1^*$$

$$M_1^* + M_2 \xrightarrow{k_{12}} M_2^*$$

$$M_2^* + M_1 \xrightarrow{k_{21}} M_1^*$$

$$M_2^* + M_2 \xrightarrow{k_{22}} M_2^*$$

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

The composition of a copolymer cannot be determined by the homopolymerization rates of the two monomers.

Assume the chemical reactivity of the propagating chain in a copolymerization to be dependent on the monomer at the growing end.

Reactivity Ratios for Styrene / POSS-Styrene

$$r_1 = \frac{k_{11}}{k_{12}}$$

$$r_2 = \frac{k_{22}}{k_{21}}$$

Alternating Copolymerization: $r_1 = r_2 = 0$

Block Copolymerization: $r_1 > 1$, $r_2 > 1$

Random Copolymerization: $r_1 r_2 = 1$

Reactivity Ratios calculated using the copolymer composition equation:

$$F1 = \frac{(r_1 f_1 f_1 + f_1 f_2)}{(r_1 f_1 f_1 + 2 f_1 f_2 + r_2 f_2 f_2)}$$

r_1 = reactivity ratio for styrene
r_2 = reactivity ratio for POSS-styrene
F_1 = mole fraction of styrene in copolymer
f_1 = mole fraction of styrene monomer in feed
f_2 = mole fraction of POSS monomer in feed

Reactivity Ratios: Challenges

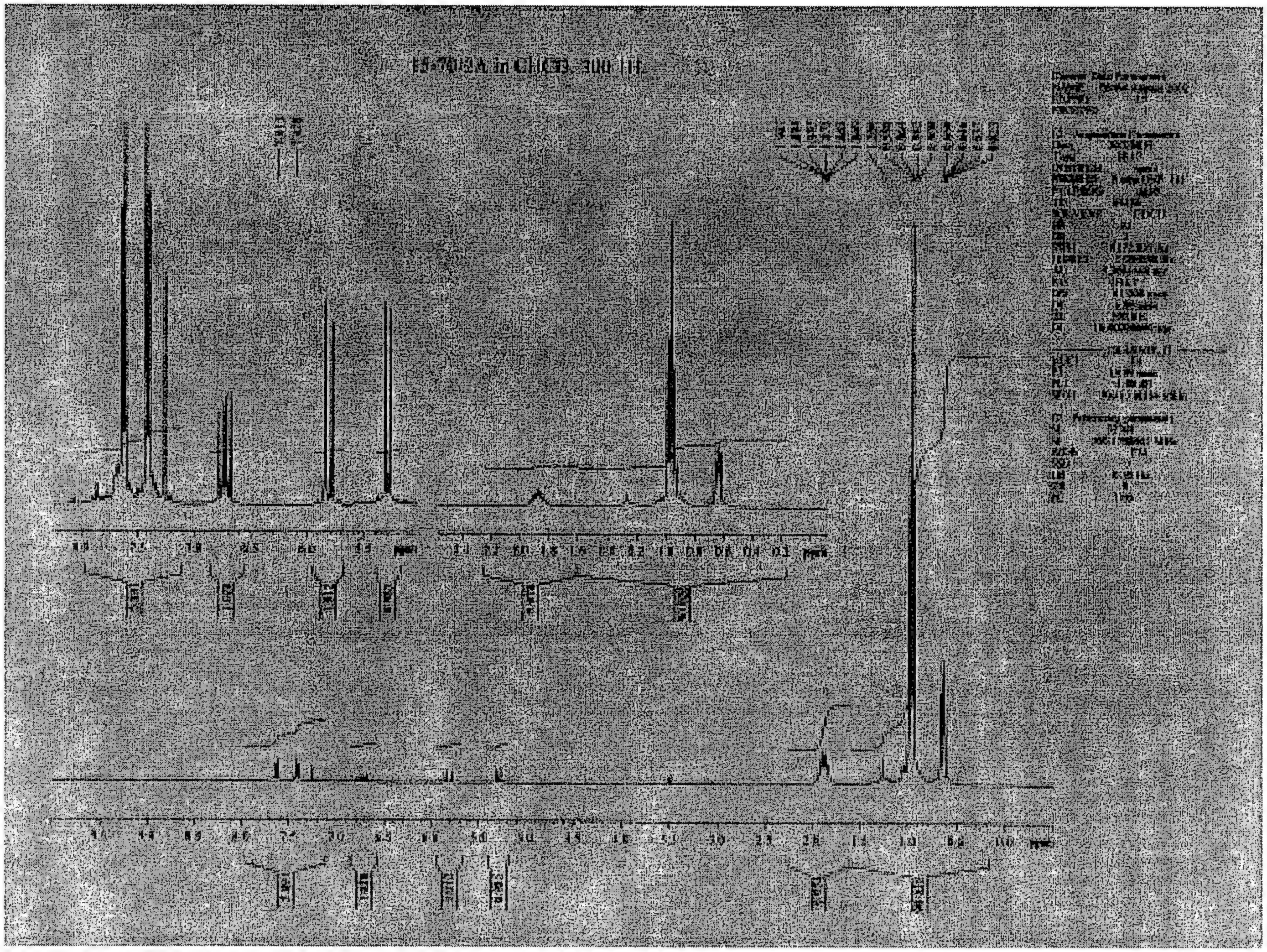
- Polymerizations <u>must</u> be carried out to only 3-5% completion.
  -Reactions were run for 3 hours and monitored by ^{1}H NMR.

- The small amount of polymer formed (a solid) must be separated from unreacted POSS-monomer (also a solid).
  -Achieved with precipitation of polymer using ether/MeOH

- Accurately determine the amount of POSS in each copolymer.
  -IR analysis much more accurate than NMR integrations.

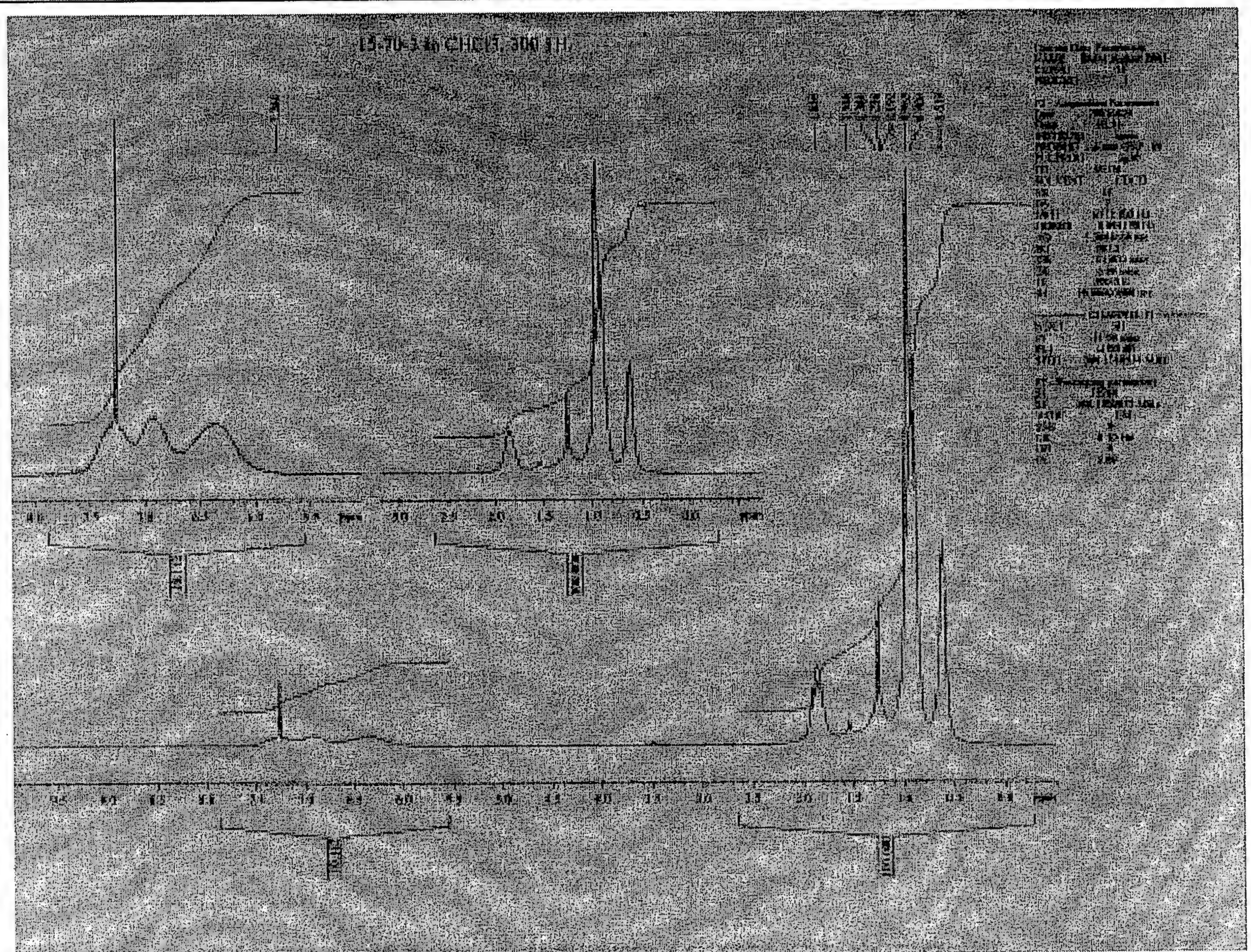
- Carry out a full (10-90) range of mole % POSS reactions while maintaining the same concentration of monomers and initiator.
  -Achieved best with isoButylPOSS as it has favorable solubility.

NMR Spectra of Crude Reaction Product



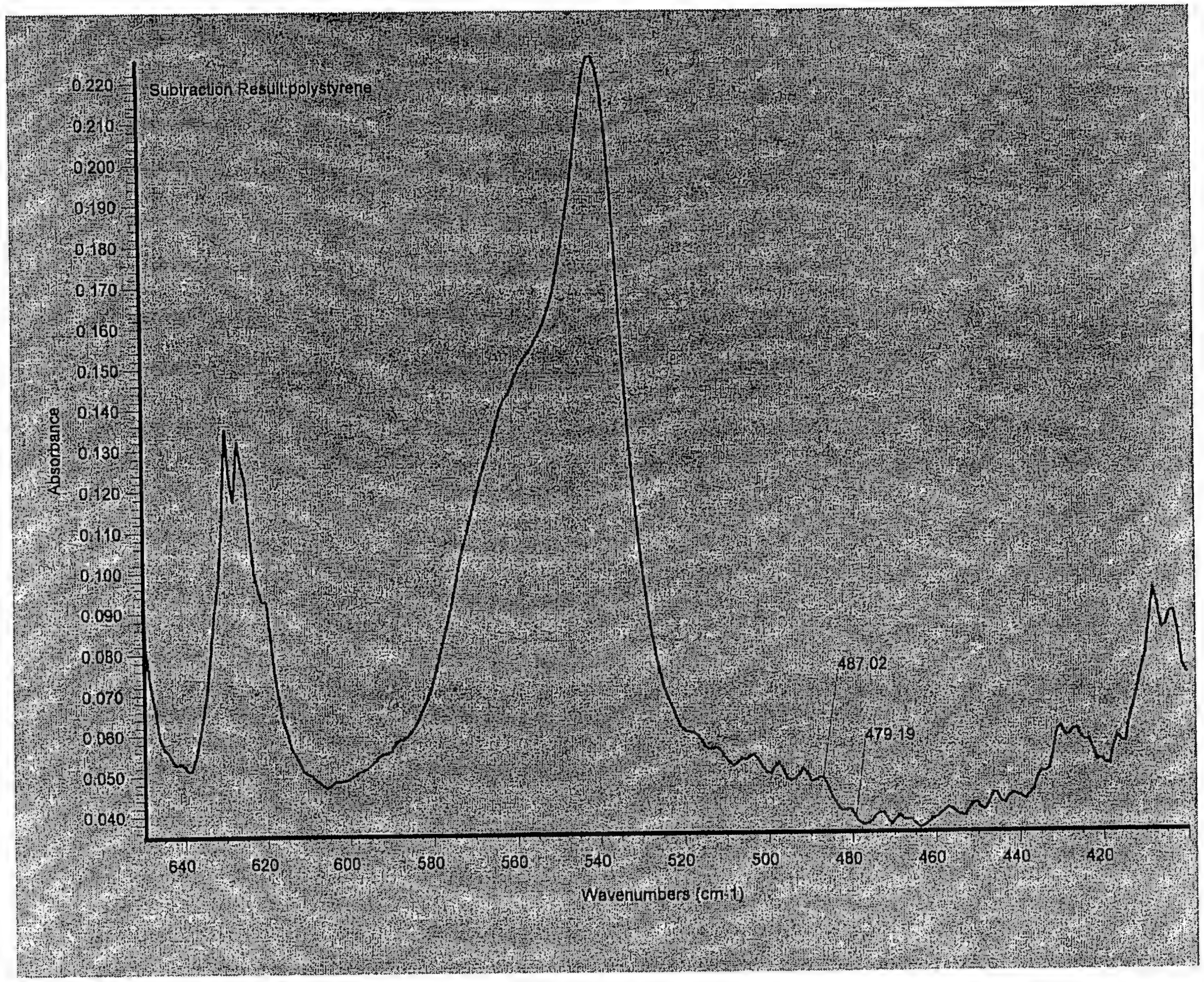
This spectrum shows mostly POSS-monomer with some copolymer

NMR Spectra of Isolated Copolymer



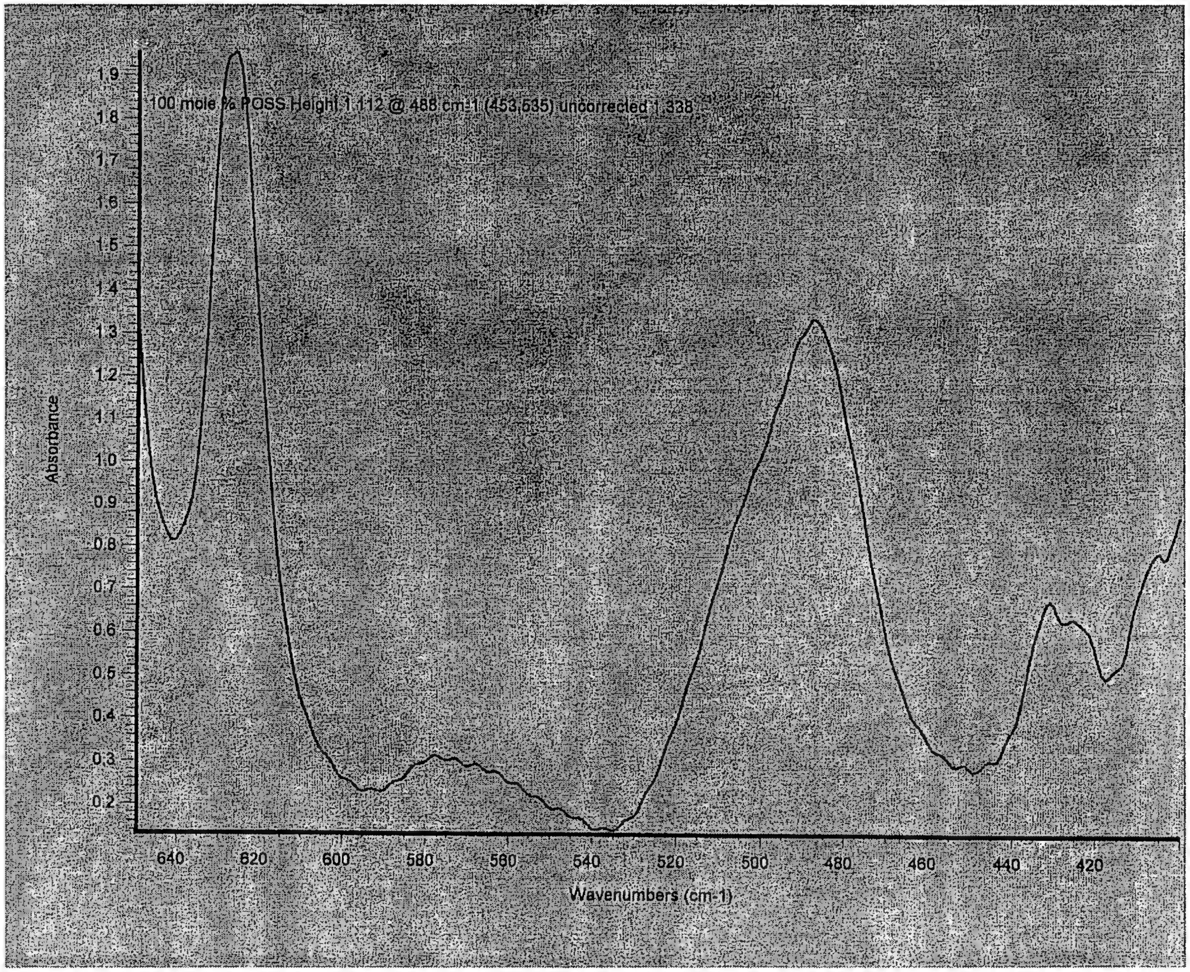
This spectrum shows monomer-free copolymer

Infrared Spectrum of Polystyrene



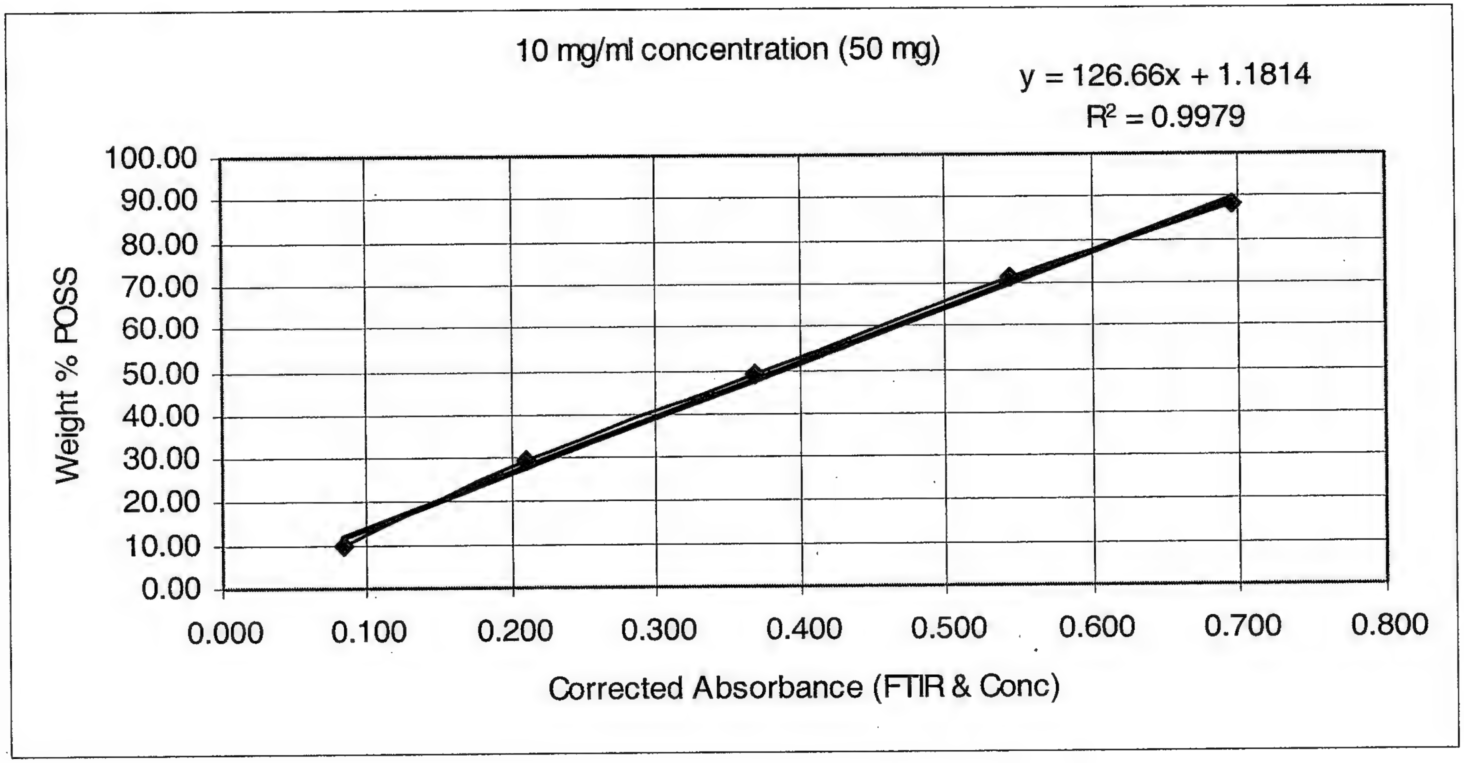
Polystyrene has no absorbance at 483 cm^{-1}

Infrared Spectrum of POSS-Styrene



An iButyl POSS-Styrene cage has a Si-O stretch at 483 cm-1

IR Calibration Curve for POSS Standards



Reactivity Ratio For POSS-Styrene

r_1 Styrene = 1.05
r_2 POSS-Styrene = 0.94

These reactivity ratios were determined by non-linear least squares analysis of nine copolymerizations.

We had two variables (r1 and r2) and 36 pairs of equations to analyze

SUMMARY

The successful incorporation of nano-sized inorganic clusters (POSS) into a variety of polystyrene copolymers has been demonstrated.

A degree of control over molecular weight can be made using standard kinetic polystyrene parameters.

Reactivty ratios show the POSS-styrene to be less reactive than styrene itself; a copolymer sequence should be close to random.

These POSS clusters have a remarkable effect on the thermal transitions and mechanical properties of the polymers they are copolymerized into.

The POSS effect on the properties of analogous polymers shows a dependency on the type of alkyl group on the POSS cluster.

TEM images of randomly copolymerized polymers illustrate this dependency, as the size of the POSS domains are alkyl-group dependent.

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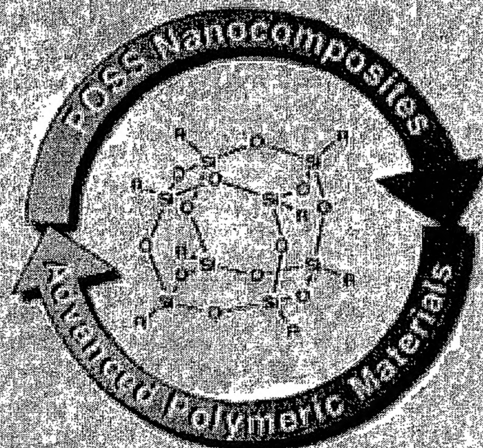

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MEMORANDUM FOR PRS (In-House Contractor Publication)

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SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2002-211**
Brian Moore; Timothy Haddad (ERC) et al., "POSS Polystyrene Copolymers, Reactivity, and Control" (viewgraphs)

POSS Nanotechnology Conference **(Statement A)**
(Huntington Beach, CA, 25-27 September 2002) **(Deadline: 25 Sept 02)**